

AN ABSTRACT OF THE THESIS OF

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Title: New Approaches for Analyzing White Pitch Deposits
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Derivatives.

Signature redacted for privacy.

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Christopher J. Biermann

White pitch deposits originated from the wood extractives, synthetic polymers, and additives used in the papermaking process, etc. may cause numerous problems to the papermaking process and also degrade the product quality. The timely analysis and characterization of white pitch deposit is important for tracing the origin of the deposits. Despite the severity of problem of white pitch deposits, there is little information on analysis of these contaminants. Gas chromatography (GC), size exclusion chromatography (SEC), proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), and fourier transform infrared spectroscopy (FTIR) were used to separate the complex constituents and identify the functional groups of the white pitch deposits. GC analysis based on retention time allowed

to determine paraffin wax, polyethylene wax, wood pitch residues, and certain additives such as rosin. Hot-melt adhesives and cis-1,4-polyisoprene were separated by SEC based on molecular weight and verified by FTIR and $^1\text{H-NMR}$. By using instrumental analysis technique can analyze the complex white pitch deposits and trace the origin of those.

Grafting of synthetic polymers onto cellulose and its derivatives is a useful way to improve their qualities and to expand the range of their uses. To date there are a few useful reaction schemes to prepare for the new classes of materials with the advantages of both material. Most of the proposed grafting reactions are carried out by free radical mechanisms. But these procedures have some inherent disadvantages. So in this study acylation reaction mechanism was adopted to achieve a high level of control compared to free radical reactions over the grafting reaction. Ethylene/maleic anhydride copolymer (EMA) and styrene/maleic anhydride copolymer (SMA) were grafted onto cellulose acetate (CA) and methyl cellulose (MC) in a simple and effective way under homogeneous reaction conditions. In addition to pyridine, N-methylimidazole (NMID) and 4-(N,N-dimethylamino)pyridine (DMAP) were used as catalysts to increase greatly the yield and rate of esterification.

New Approaches for Analyzing White Pitch Deposits and
Grafting of Synthetic Polymers onto Cellulose Derivatives

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New Approaches for Analyzing White Pitch Deposits and Grafting of Synthetic Polymers onto Cellulose Derivatives

CHAPTER I

Analytical Techniques for Analyzing White Pitch Deposits

LITERATURE REVIEW

Secondary fiber is a fiber source from recycled paper and is an effective substitute for wood and nonwood pulp fibers. Use of recycled paper also decreases the solid waste problem. Paper contributes up to 40% of solid waste¹. The recovery and utilization of waste paper have increased in some countries since the early 1970's and it is widely expected that this trend will increase in the future. Thus waste paper will be used in more grades of paper and in higher percentages.

Recycled fiber has been an importance source in the United States and Europe for many years and some detailed studies have been published²⁻⁶. In Europe the waste paper recovery rate is already 35 % of the fiber supply. The use of waste paper as a fiber source for papermaking in the United States totalled 13.5 million tons in 1973, representing only 18.8 % of total fiber sources⁷. Waste paper as a fiber resource in papermaking has become progressively more important and exports of waste paper have increased rapidly since that time. As a result, the waste paper recovery rate has increased steadily throughout the

1970's and 1980's. The American Paper Institute (API) reports that the paper industry in the United States consumed about 18.7 million tons of waste paper in the production of paper and paperboard, representing 26.5 % waste paper recovery rate relative to paper and paperboard production in 1989⁷.

During 1989, domestic collection of waste paper in the United State totalled 25.0 million tons, of which 5.7 million tons were exported to South Korea, Mexico, Taiwan, Japan, Canada, Spain, Italy, and the Philippines⁸. This trend will be continued to at least the year 2000. The American Paper Institute reports that the pulp and paper industry in the United States set an ambitious goal for waste paper recovery rate for 1995. The new waste paper recycling goal is 40 % by 1995, which represents 40 million tons, an increase of 50 % over 1988 levels⁸.

Waste paper suitable for recycling consists of various grades. Books and documents tend to have a long life and are rarely used as a fiber sources for recycling. The best grades for recycling are mainly telephone directories, newspaper, magazines, printed advertising material, carton boards, and corrugated containers. The most desirable raw materials are acquired from printing waste. Almost 100 % of these products are recyclable. Other important sources of waste paper supply are department stores, supermarkets, and other enterprises, industrial units, converting plants, and

offices. Waste paper is generally classified and priced according to quality, starting with higher quality (white clippings, newspapers, magazines) worth about \$300/ton and ending with mixed unsorted waste worth \$10-\$25/ton. One important element in recycled paper is to have uniformity of product without contamination. For example, newsprint should not be bound with brown paper.

Even though paper recycling in the United States is on the rise and penetrating into the manufacture of newsprint, waste paper-based linerboard, corrugating medium, tissue, writing and printing paper, recycling mills are experiencing increasing difficulty with troublesome sticky contaminants in wastepaper originating from the hot melt adhesives used widely in packaging and book bindings, pressure sensitive adhesives as used on tapes and labels of numerous types, polystyrene foam used as a packaging insert or in other products such as disposable trays and cups, and synthetic and natural fibers used to bundle old newspapers. These contaminants have significant adverse impact on either paper mill operations or the finished product quality. Contaminants from secondary fiber are causing serious problems to the paper industry as the amount of paper being recycled and the amount of synthetic polymers in paper products both increase. Deposits on screens, paper machine wires, and felts results in reducing the mill capacity by causing a slowdown of the machine or downtime for cleanup purpose.

Perhaps the most serious effect of contaminants is lower product quality. Apart from the immediate effect of customers dissatisfaction, a reputation of low quality is established for that particular product. This undoubtedly leads to economic penalties. A more detailed classification and problems of these contaminants in papermaking have been provided by Franklin et al. earlier⁹. Recently types of adhesives found in white pitch deposits have been reviewed by Moreland¹⁰ and Savil¹¹.

Considering the serious problems caused by white pitch deposits in the paper mill, the analysis and characterization of contaminants are very important for a basic understanding of contaminant problems and for tracing the origin of contaminants. Even though sophisticated analytical techniques have the drawback that some time is required to obtain results, and are not particularly useful to solve the problem immediately, their use should not be overlooked because they can give information that may prevent the problem from recurring.

Despite the severity of the problems of white pitch deposits, only a few papers on analyses of these contaminants have been published. Some useful papers have appeared recently on proton nuclear magnetic resonance (¹H-NMR) spectroscopy¹², carbon nuclear magnetic resonance (¹³C-NMR)^{13,14}, fourier transform infrared (FTIR) spectroscopy^{15,16}, gas chromatography mass spectroscopy (GC-MS)^{16,17}, pyrolysis-

gas chromatography (Py-GC)^{16,18,19}, size exclusion chromatography (SEC)^{14,17,20}, and a variety of other techniques²¹. Each of these techniques has advantages and limitations with respect to sample size and type, sensitivity, equipment requirements, and sample handling.

A. Proton nuclear magnetic resonance(¹H-NMR).

This technique has the potential to allow qualitative and quantitative analysis. Quantitative application of ¹H-NMR spectroscopy have greatly contributed to the compositional analysis of high polymeric materials. Analysis of white pitch deposits by ¹H-NMR is a quick method to get detailed structural information from other techniques such as FTIR. ¹H-NMR spectra are relatively simple compared to FTIR spectra, though their analysis requires a detailed knowledge of structural organic chemistry. The ¹H-NMR spectra indicates what type of functional group each hydrogen atom belongs. The measured response is a chemical shift, expressed in dimensionless unit δ or parts per million (ppm), relative to the hydrogen atoms of the standard reference compound tetramethylsilane (CH₃)₄Si, also called TMS. ¹H-NMR gives a peak area for each type of hydrogen atom that is proportional to the amount of that hydrogen atom. For example, -CH₃, -CH₂, -CH₂-R, CH₂-X, and -CH have characteristic chemical shift and peak area of 3:2:2:2:1, respectively.

B. Fourier transform infrared spectroscopy (FTIR).

A transmission infrared spectrum of an opaque sample such as paper and some sticky can be recorded on the FTIR spectrometer. The FTIR spectrometer has higher energy throughput than the dispersive infrared spectrometer and the resolution of the spectrum can be much improved by using a beam condenser to send more signal to the detector. The high signal-to-noise ratio of FTIR makes possible the quantitative determination of the weak infrared absorption of the white pitch deposit in paper mill. It was reported by Jayme and Traser²² that infrared spectroscopy can be used to determine the identity of paper mill deposits. One year later Bogatie²³ reported that infrared spectroscopy can be used for identifying paper mill deposits. Furthermore, the sensitivity of the method can be improved in some samples by extracting the contaminant with a nonpolar solvent and evaporating the solvent to isolate the contaminant.

C. Size exclusion chromatography (SEC).

The rapid development of detectors and high performance packings for size exclusion chromatography (SEC) during this decade has led to increased use of SEC for rapidly determining the molecular weight and the molecular weight distribution of polymers. It is known that separation by SEC, which was developed by Moore²⁴, is based on molecular size²⁵. SEC should be a useful tool for analysis of pitch

deposits. SEC has several advantages over other methods such as GC, IR, or NMR. The analysis is carried out at room temperature and a complete analysis of components is made in a single experiment. No pretreatment of the sample, such as esterification, is required. The original constituents of the sample are not destroyed and can be recovered for subsequent identification by established techniques such as gas chromatography, fourier transform infrared spectroscopy, and nuclear magnetic resonance spectroscopy.

D. Gas Chromatography (GC).

Gas or vapor phase chromatography has been extensively used in identifying the thermal decomposition products of compounds. The term "gas chromatography" includes all chromatographic techniques in which a mobile gas phase carries substances to be separated through a stationary phase packed into a suitable column. Gas-liquid chromatography was suggested by Martin and Synge²⁶ in 1941 and demonstrated through the experiments of James and Martin in 1952²⁷. An excellent review has been published by Hardy and Pollard²⁸. Gas chromatography was employed for determining resin acids and fatty acids in a sophisticated methods^{29,30}.

Three important factors can be considered in obtaining precise results, even though the success in the separation and identification of compounds depends upon various instrumental factors, experimental procedures, and operator

technique. The three factors are carrier gas, column efficiency, and detector. The carrier gas must be inert; argon, nitrogen, hydrogen, or helium are usually used, especially the latter two with capillary columns. The efficiency of the column (often reported as theoretical plates) depends upon its dimensions, the amount of stationary liquid, the thermal stability and physical properties of the stationary liquid, and the nature of the solid support in general. The ideal requirements for a detector are high sensitivity to the presence of a component in the carrier gas, rapid response, linear response, and good baseline stability. Differential detectors used to be widely used and are based on thermal conductivity measurements. However, the flame ionization detector³¹ or the capillary tube detector³² are now the most commonly used detectors due to their high sensitivities and linear response.

INTRODUCTION

The increased use of secondary fiber and synthetic polymers in papermaking and the increasingly closed water cycle of paper machines contribute to the formation of pitch, stickies, and other contaminants on paper mill equipment. These deposits often contain many components that further complicate the picture because they may originate from the wood extractive components appearing in the pulp - especially pulp from resinous species such as aspen (Populus tremuloides Michx.)³³ or southern pine, additives used in the papermaking process, polymers from secondary fiber sources, and other sources, or mixtures of these. Table I-1 shows the sources, types, and original uses of contaminants found in the paper mill as well as effects of these materials on the papermaking and paper. The preferred generic term used for the cause of paper spotting and paper mill residue deposits is "white pitch deposits," regardless of the source of the contaminants - whether wood pitch, additives used in the process, or contaminants from secondary fiber. The buildup of contaminants on paper machines and paper products is a significant problem. In kraft mill the worst deposition is usually in the unbleached screen room on the walls of pipes, the surfaces of vats, the screen plates, the brownstock decker apron, and the repulper screw. Even though the agglomerations sometimes plug screen slots and cleaners, more serious

Table I-1. Major white pitch contaminants found in recycling mills.

Source	Contaminants	Original uses and problems in mill
Secondary fiber	Hot melt adhesive	Sealing, bookbinding (EVA); defects in products
	Polystyrene foam	Packing; stick to rolls, indent sheets
	Pressure sensitive adhesive	Case sealing, splicing rolls (natural rubber); stick to felts and wires, deposits on dryers
	Wax	Paperboard laminate and coating; degrade products
Wood Pitch	Fatty acid	Wood pulp/ nonvolatile component
	Rosin (resin acid)	Wood pulp/ nonvolatile component
	Sterol	Wood pulp/ diterpene in softwoods
Within Mill	Rosin	Sizing agent
	Fatty acid	Defoamer
	Polymers	Splicing tape additives

problems happen when the agglomerations break away from their surfaces of attachment because they are chopped up by pump impellers, agitators, etc., and gives finely dispersed debris in the final product. Contaminants from secondary fiber are causing more serious problems to the paper industry as the amount of paper being recycled and the amount of synthetic polymers in paper products both increase. Deposits on screens, paper machine wires, and felts results in reducing the mill capacity by causing a slowdown of the machine or downtime for cleanup purpose. Furthermore, a single piece of paper machine clothing may cost \$100,000. Perhaps the most serious effect of contaminants is lower product quality. Apart from the immediate effect of customers dissatisfaction, a reputation of low quality is established for that particular product. This undoubtedly leads to both economic penalties and a low quality psychology.

Considering the serious problems caused by white pitch deposits in the paper mill, the analysis and characterization of contaminants are very important for a basic understanding of contaminant problems and for tracing the origin of contaminants. In fact, it is not easy to trace the origin of white pitch deposit in a particular mill situation. Due to the limitations of analytical instrumentation at mills or the long delay in analysis from the corporate technical centers, most paper machine operators can only modify certain operating procedures to solve the problem, only to have it

reappear at another time.

Despite the severity of the problems caused by white pitch deposits, only a few papers on analyses of these contaminants have been published. Some useful papers have appeared recently on proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy¹², carbon nuclear magnetic resonance ($^{13}\text{C-NMR}$)^{13,14}, fourier transform infrared (FTIR) microscopy^{15,16}, gas chromatography mass spectroscopy (GC-MS)^{16,17}, pyrolysis-gas chromatography (Py-GC)^{16,18,19}, size exclusion chromatography (SEC)^{14,17,20}, and a variety of other techniques²¹. Each of these techniques has advantages and limitations with respect to sample size and type, sensitivity, equipment requirements, and sample handling. However, there are some common analytical techniques available that are quite useful for characterizing mill deposits, techniques that have not been discussed in detail in the published literature. Among these are gas chromatography (GC) and size exclusion chromatography (SEC). Also, general strategies for white pitch analysis should be considered.

The methods for separating and identifying components of paper machine contaminants were studied for determining the origin of the contaminant, for monitoring the effectiveness of combative measures and additives, and for other purposes. Of the available characterization methods, $^1\text{H-NMR}$, FTIR, GC, and SEC have been used extensively in this work. Used together, these techniques allowed a precise characterization

of mill residues. The features of these techniques are summarized in Table I-2.

There has been little work on comprehensive analysis of white pitch residues in conjunction with pitch abatement schemes or the use of pitch-controlling additives. For example, are all of the components of pitch decreased by additives such as talc, or are some components easier to control than others by a certain method? What additives contribute to the problem? Do sticky scavengers³⁴ work on all sources, or does it depend on the contaminant's structure and molecular weight? Fundamental research will have to be carried out in this area to reduce the difficulty caused by white pitch deposits.

RESULTS AND DISCUSSION

The techniques for characterizing white pitch deposits can be divided into those that separate the components (involving chromatography) and those that do not. This distinction is important for white pitch deposits that are complex mixtures of contaminants from various sources. Two methods considered here that actually separate the constituents of white pitch deposits are gas chromatography (GC) and size exclusion chromatography (SEC). The other methods, in Table I-2, are used to characterize the complex pitch or individual constituents after separation by size exclusion chromatography.

A. Sample collection and purification.

The first step in white pitch analysis is to obtain samples. Sometimes the mill has a general buildup of a contaminant on paper machine felts or wires that has caused a shutdown for cleaning or replacement. If the wire or felt is replaced, then a sample can be sent to the lab; if not, some of the material scraped from the wire is sent to the laboratory. In some cases, one may want to analyze several individual samples collected at one time or over a period of time to see if there are multiple sources.

Unless set by heat (as in paper spots), white pitch deposits are almost always soluble in nonpolar solvents such

Table I-2. Descriptions of separation and analysis instruments.

Methods	Features	Remarks
SEC	Separation by molecular weight; nondestructive	Soluble compounds; fractions can be analyzed separately
GC	Separation and identification by retention time	Volatile compounds (waxes, wood pitch, fatty acids, rosin)
¹ H-NMR	Identification of proton numbers	Soluble compounds with hydrogen atoms
FTIR	Identification of functional groups	All compounds; not quantitative

SEC : Size exclusion chromatography

GC : Gas chromatography

¹H-NMR : Proton nuclear magnetic resonance spectroscopy

FTIR : Fourier transform infrared spectroscopy

as toluene, chloroform, or methylene chloride, even though solvents such as hexane are not polar enough for most components. Therefore, these deposits tend to be nonpolar molecules themselves. When the residues of small sections of wires or felts are extracted with one of these solvents, followed by filtration of the solution and evaporation of the solvent in the filtrate, white pitch free of entrained fibers, talc, and other materials can be obtained. This simplifies its analysis.

B. Gas chromatographic (GC) analysis.

The main function of gas chromatography (GC) is to separate and identify unknown compounds on the basis of retention time. Therefore, other constituents of white pitch samples do not interfere with the analysis, and both qualitative and quantitative information can be derived. A small amount of sample mixture is dissolved in a small volume of solvent and injected by syringe into a heated inlet of the gas chromatography. The sample is instantly vaporized and is then swept through a heated chromatography column by a stream of carrier gas. Gas chromatography analysis of white pitch deposit, therefore, is limited to those components that can be made volatile at temperatures below about 300°C. It is useful for petroleum wax, extractives, and certain low molecular weight additives. For those compounds with polar groups such as R-COOH and R-OH, for example, the fatty acids,

resin acids, and sterols from the wood extractives (Figure I-1), it is necessary to derivatize the components to increase their volatility. A convenient and multipurpose derivative is the trimethylsilyl derivative; the formation of these derivatives is called "trimethylsilylation," or "silylation" for short. Silylation is a common, simple laboratory technique. The trimethylsilyl derivatives are formed as follows:

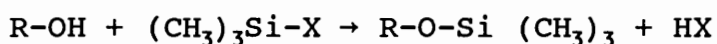
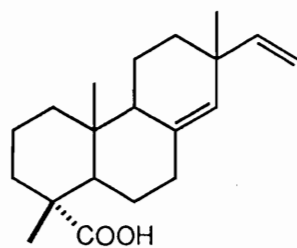


Figure I-2 shows a wood pitch sample separated on a packed column using ion monitoring³⁵. In this case, palmitic acid elutes at 13.4 min., margaric acid at 14.2 min., C-18 fatty acids at 15.2 min., resin acids from 15.5 min. to 19.5 min., and sterols from 23 min. to 25 min. In a particular mill, samples of pitch from each species of wood, commercial rosin, and other suitable materials would be analyzed for comparison with contaminants collected at the mill. In a related method, tall oil constituents were methylated with diazomethane prior to analysis by gas chromatography using a capillary column³⁶. Studies that give the composition of pitch from various species of wood are useful if one's mill uses those species; however, there is relatively little information available on capillary gas chromatography of wood pitch. Also, the fact that the composition of extractives

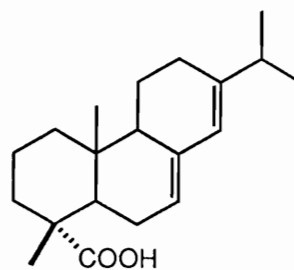
changes during pulping and bleaching complicates the picture. Various types of wax can be analyzed directly after hexane extraction of the white pitch. There are three important types of wax (Figure I-3) that can be distinguished:

1. Paraffin wax, a series of simple alkanes from C-25 to C-40.
2. Wax made from ethylene, which contains even-number chains of simple alkanes.
3. Microcrystalline wax, which has a higher molecular weight than paraffin wax and contains branch.

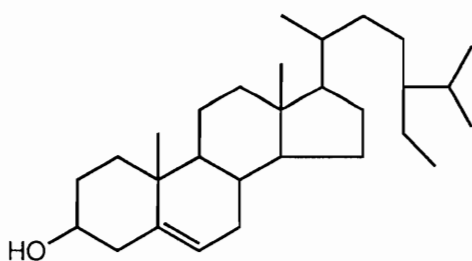
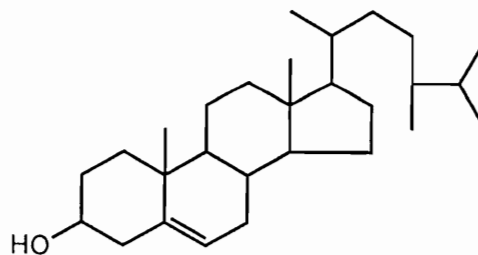
Figure I-4 shows chromatograms of paraffin wax and polyethylene wax, respectively, separated on a capillary column with naphthalene (the first peak after the solvent) as an internal standard. Because gas chromatography separates the components and the components are identified on the basis of retention time, other constituents of pitch samples do not interfere with the analysis. Both qualitative and quantitative information can be derived, which would be impossible for spectroscopic methods. For example, the distribution of fatty acids in wood pitch (or from defoamers) can be used to characterize the species or source. Microcrystalline wax contains branched aliphatic moieties that can be distinguished from paraffin wax through the technique of gas chromatography. Also, hydrogenated resin acids used in hot



Dextropimaric Acid



Abietic Acid

 β -Sitosterol

Campesterol

Figure I-1. Chemical structures of selected wood extractives.

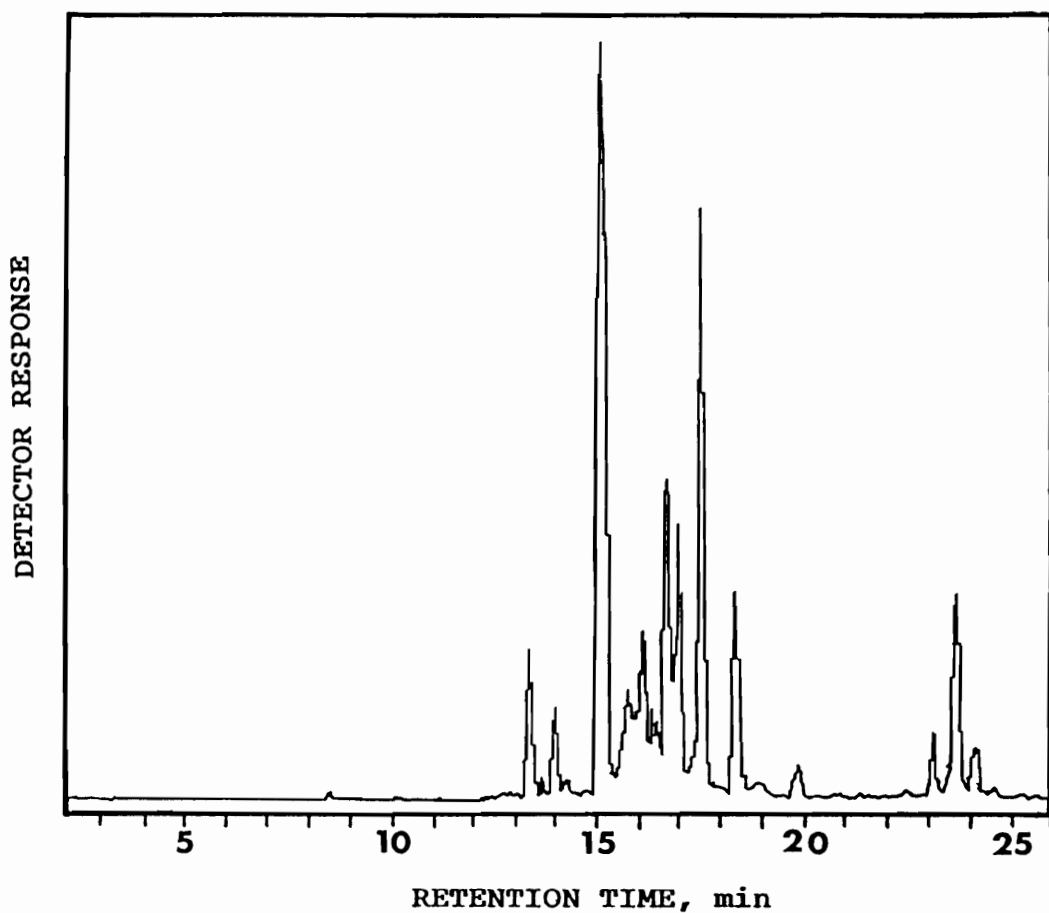


Figure I-2. GC chromatogram of typical trimethylsilylated tall oil samples from pine on a GC packed column showing fatty acids, resin acids, and sterols.

melt adhesives can be distinguished from resin acids from wood pitch or rosin sizing agents.

Some compounds coelute, meaning that they have the same retention time, which precludes gas chromatography as the method of analysis. For these, mass spectroscopy can be used to figure out the identity and quantity of the individual components. For example, the trimethylsilyl derivatives of the C-18 fatty acids -- stearic, oleic, linoleic, and linolenic acids (Figure I-3) -- all coelute on packed columns, but their trimethylsilyl derivatives can be determined separately

by monitoring the ions at 341, 339, 337, and 335 nm, respectively. (On capillary columns, stearic acid can be resolved from the other three components, having a slightly longer retention time.) Analyzing these separated materials by gas chromatography allows one to determine the presence in the contaminant of paraffin wax, certain other waxes, pitch originating from wood extractives (with much information on the actual or likely species of wood), defoamers containing fatty acids, calcium stearate used as an additive, and rosin added in the papermaking process.

C. Analysis by size exclusion chromatography (SEC).

Size exclusion chromatography (SEC) analysis is the only other convenient method available to separate the components of paper mill deposits. SEC columns for this purpose are

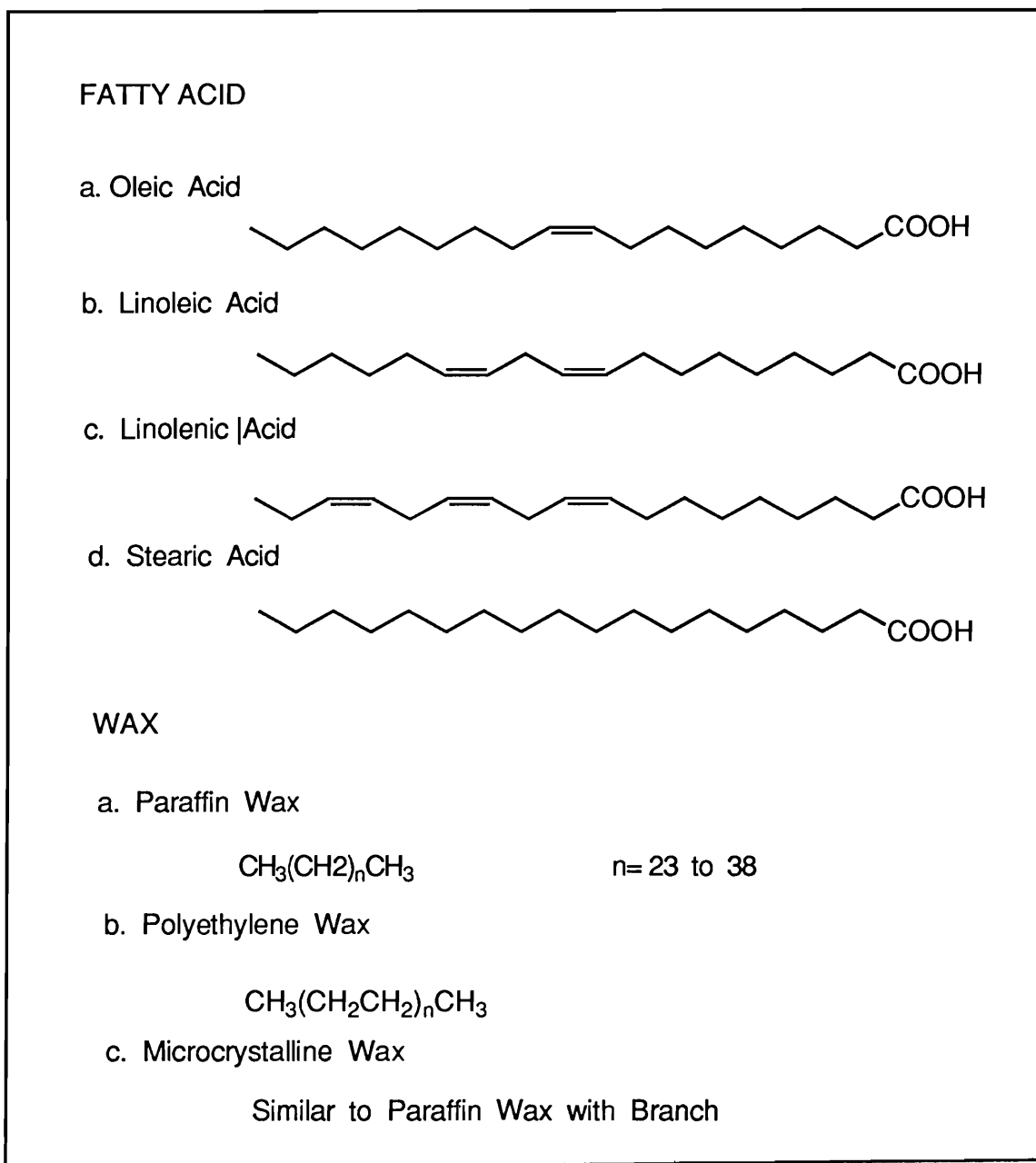


Figure I-3. Structures of selected fatty acids and waxes.

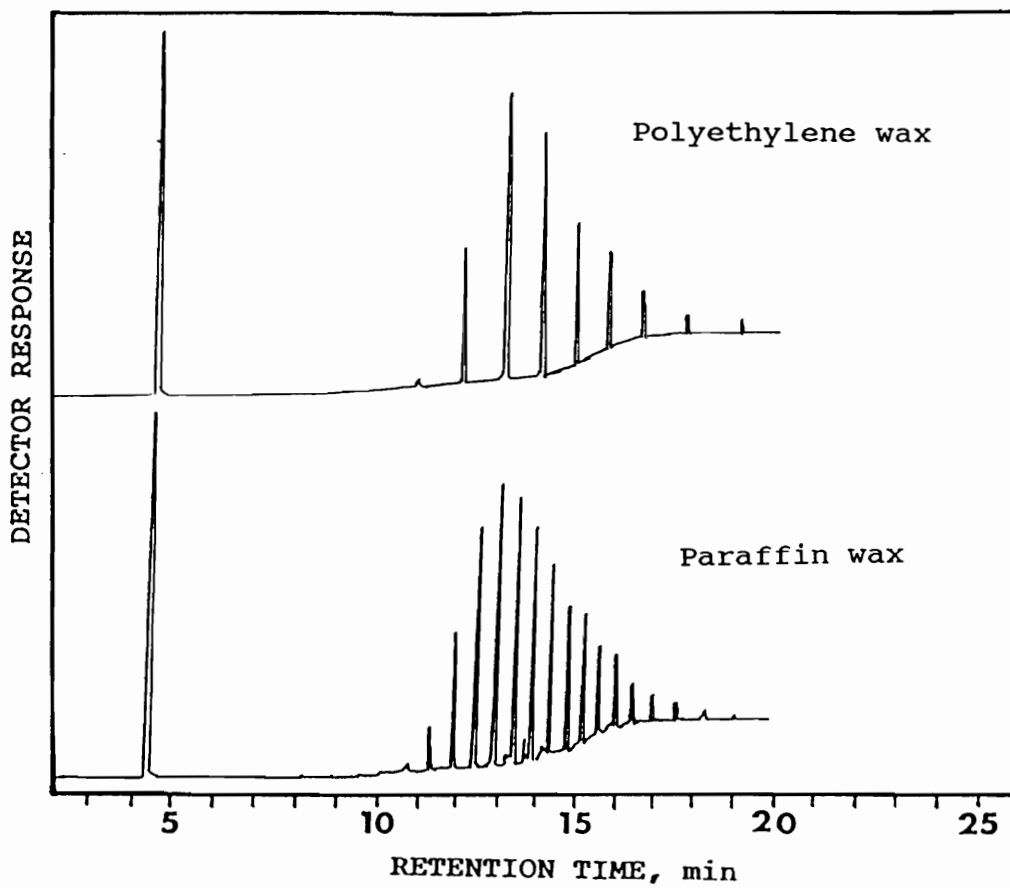


Figure I-4. GC chromatograms of paraffin and polyethylene waxes.

generally made of polystyrene crosslinked with various amounts of divinylbenzene to give certain pore sizes and, therefore, to separate mixtures by molecular weight (or molecular size). Large polymers cannot enter the small pores and are eluted first, a unique characteristic of SEC methods. Elution of polymers is monitored by a refractive index detector that detects all materials with approximately the same sensitivity and is plotted as positive and negative peak depending on the structure of compound coming out.

A useful approach for some samples, even though not used in this study, would be to use chloroform as the eluent (usable above 233 nm in the ultraviolet range), trap the individual peaks using a refractive index detector, and analyze the peaks on a scanning ultraviolet-visible spectrum spectrophotometer. With this approach, one can detect compounds such as polystyrene (260 nm), rosin and rosin derivatives (260-290 nm)²¹, antioxidants, and stabilizers that absorb above 233 nm in the ultraviolet range could be determined directly.

Since size exclusion chromatography is a nondestructive procedure, the separated components can be collected in a fraction collector and recovered after solvent evaporation. Later, additional analyses such as FTIR and NMR can be performed on the purified fractions without cross interference. Figure I-5 shows a SEC chromatogram of white pitch residue with a complex molecular weight distribution that

could be used to fingerprint the source; in this case, the contaminant is natural rubber cis-1,4-polyisoprene, as determined by $^1\text{H-NMR}$ analysis (Figure I-6.)

Figure I-7 shows a typical pattern from size exclusion chromatography of hot-melt adhesives. There is a modified resin peak at 10.04 monitored as positive, a wax peak (negative refractive index) at 9.28, and a polymer peak, which in this case is a branched aliphatic polydisperse polymer with a molecular weight in the vicinity of 100,000. More often, hot-melt adhesives used in the packaging and binding industries use ethylene vinyl acetate copolymer as the polymer (Figure I-8). Components such as wax and polyethylene copolymers will be separated by this technique to obtain a further detailed analysis of each component without cross interference.

D. Identification by fourier transform infrared spectroscopy (FTIR).

Fourier transform infrared spectrum gives the most information about the compound's chemical structure. A molecule is constantly vibrating and its bonds stretch and bend with respect to each other. When the molecule is irradiated with electromagnetic radiation, the vibrating bond will absorb energy from the light if the frequencies of the light and the vibration are same. A particular part of IR spectrum is referred to by frequency and expressed by in

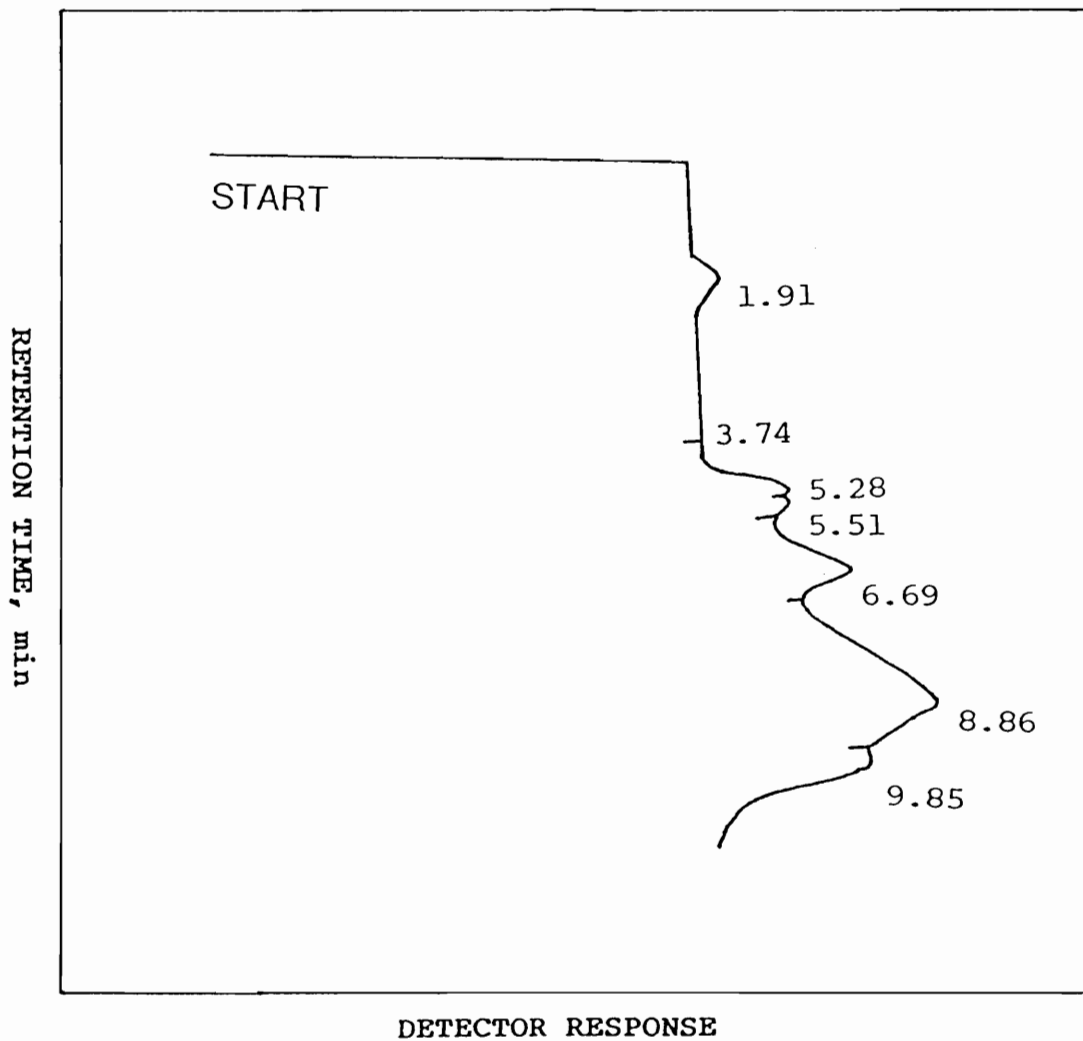


Figure I-5. SEC chromatogram of *cis*-1,4-polyisoprene.

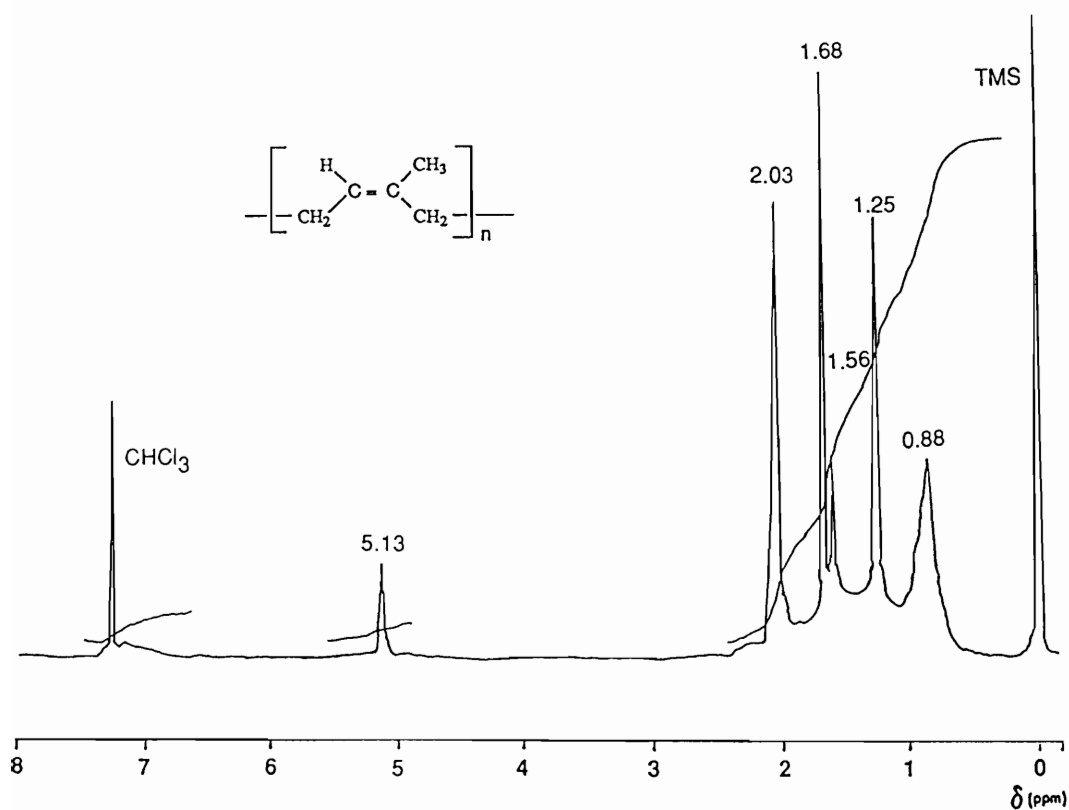


Figure I-6. $^1\text{H-NMR}$ spectrum of cis-1,4-polyisoprene.

wavenumbers- cm^{-1} , often called reciprocal centimeters. Bond intensities are expressed either as transmittance (%) or absorbance (A).

The major uses of IR as an analytical tool is to identify and to measure quantitatively specific functional groups. IR spectroscopy can give information as to types of functional groups present in a molecule because a particular group of atom gives rise to characteristic absorption bands. Both liquid and solid samples can be used for IR analysis. Figure I-9 shows a IR spectrum of cis-1,4-polyisoprene. In alkane, C-H stretching occurs to the right of 3000 cm^{-1} . On the other hand, compounds containing vinylic, acetylenic, and aromatic hydrogen have their characteristic absorption to the left of 3000 cm^{-1} . Two peaks at 2924 and 2854 cm^{-1} , therefore, shows that this compound contains a methyl group. Carbon-carbon double bonds have typical absorptions around 1600 cm^{-1} (1602 cm^{-1} in this case). The peaks at 1462 and 1377 cm^{-1} show bending of CH_2 and CH_3 , respectively. In general trisubstituted vinyl compounds have characteristic out of plane bending at $840\text{-}790\text{ cm}^{-1}$. From this data and by the NMR spectrum (Figure I-6) it can be concluded that this contaminant is natural rubber, cis-1,4-polyisoprene, used in masking and splicing tapes.

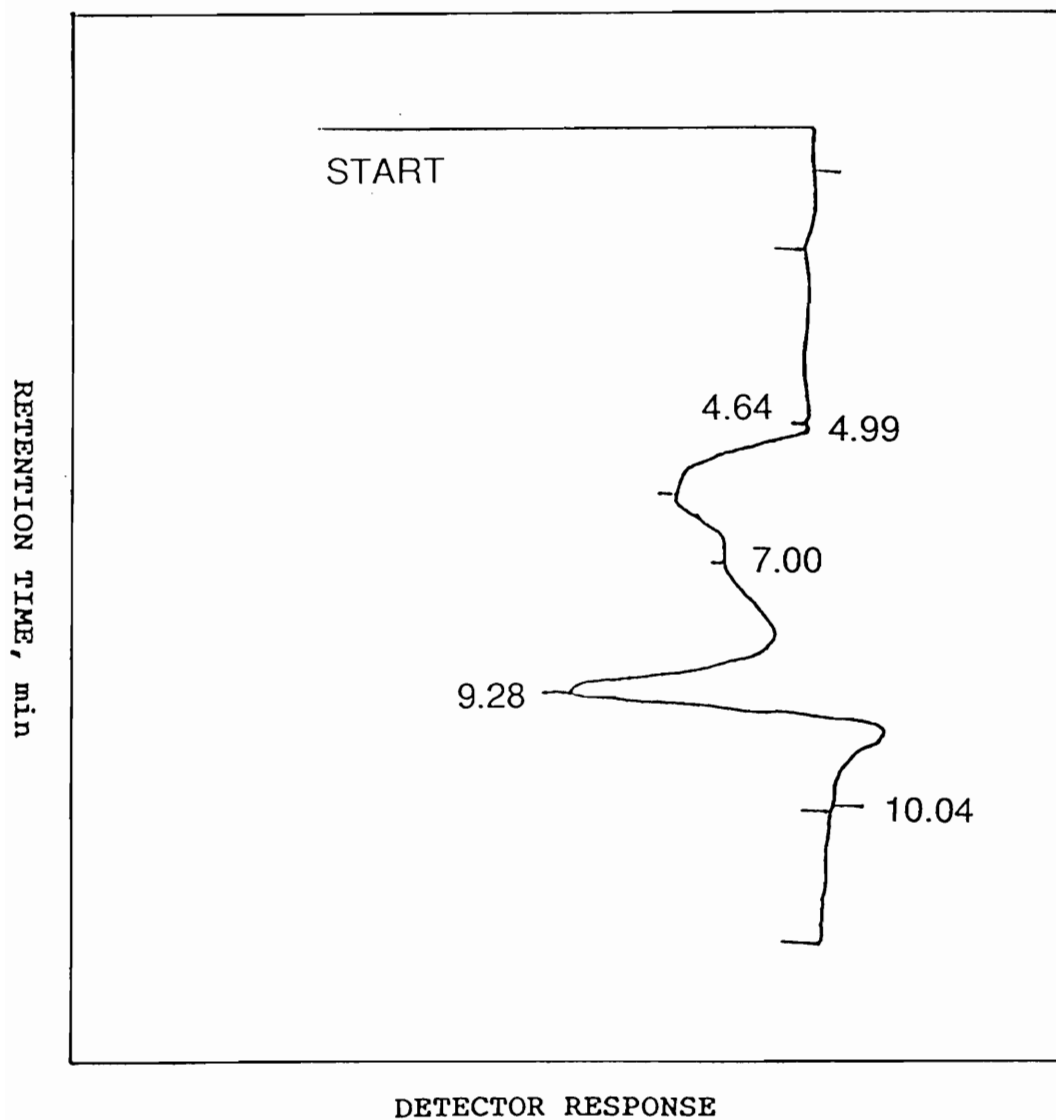
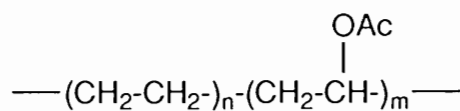


Figure I-7. SEC chromatogram of a hot melt adhesive.

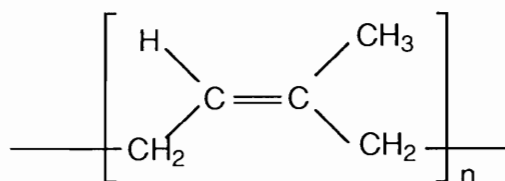
E. Identification by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$).

While FTIR spectroscopy reveals information as to the types of each functional groups present in a molecule, proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) gives information about the number of each type of hydrogen and this technique can be applied to all soluble compounds. In $^1\text{H-NMR}$ spectrum, chemical shift of each type of hydrogen relative to tetramethylsilane (TMS) is expressed by the δ unit (ppm). Proton NMR ($^1\text{H-NMR}$) gives a peak area for each type of hydrogen atom that is proportional to the amount of that hydrogen atom. For example, the $^1\text{H-NMR}$ spectrum of cis-1,4-polyisoprene (natural rubber) is shown in Figure I-6. The peak ratio of three chemical shifts at 1.68, 2.03, and 5.13 ppm in Figure I-6 is 3:4:1. The methyl group appears at 1.68 ppm as a sharp single peak, two different types of methylene groups have very similar chemical shift and overlap to produce a single peak at 2.03 ppm, and the olefin proton appears as a weak broadened triplet at 5.13 ppm. Also three extra peaks are present at 1.56, 1.25, 0.88 ppm, respectively. These three chemical shifts came from the reaction of carbon-carbon double bond in natural rubber during bleaching process. (This hypothesis was tested by exposing natural rubber to aqueous hydrogen peroxide at 160°F at pH 9 and noting an increase in these peaks.)

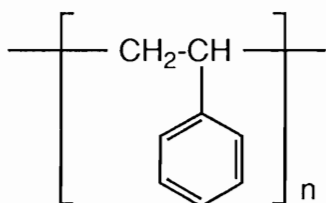
a. Ethylene Vinyl Acetate Copolymer



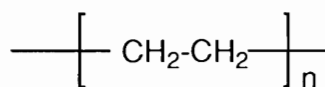
b. Cis - 1,4 - Polyisoprene (Natural Rubber)



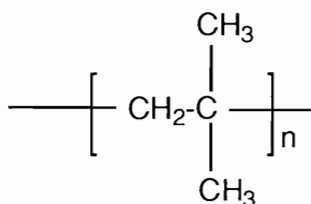
c. Polystyrene



d. Polyethylene



e. Polypropylene



f. Ethylene Isobutylene Copolymer

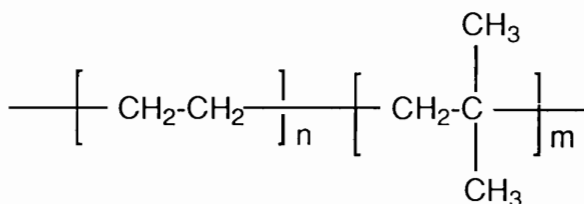


Figure I-8. Structures of polymers found in papermills.

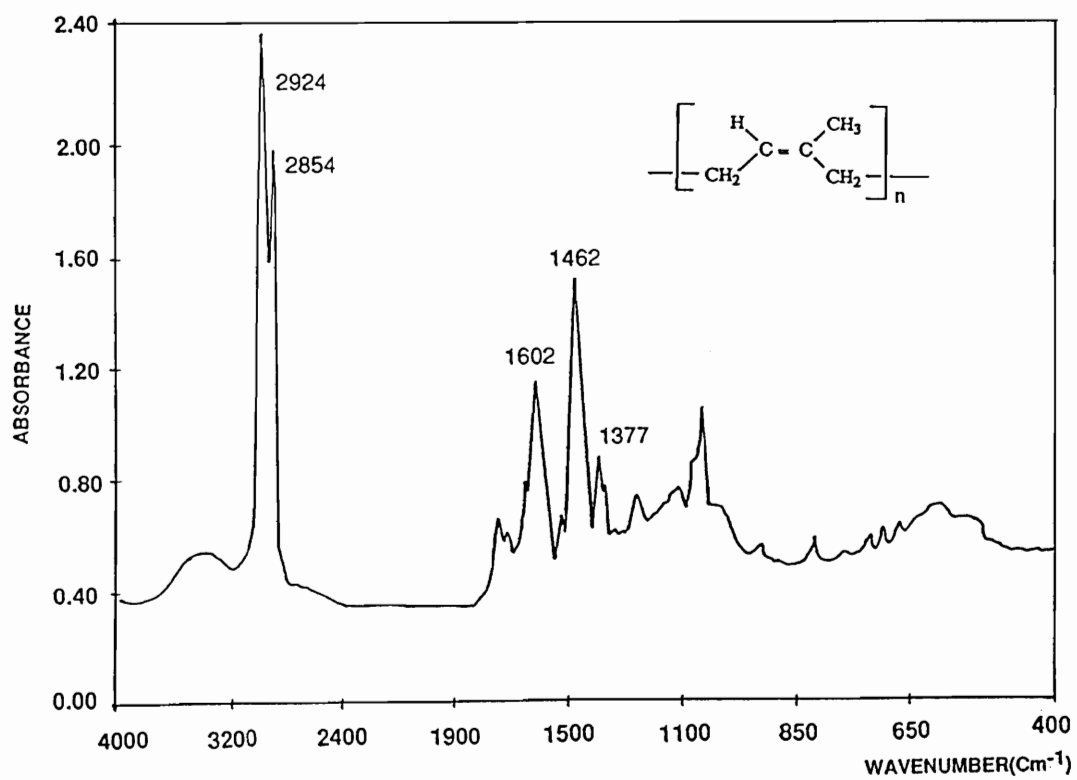


Figure I-9. IR spectrum of *cis*-1,4-polyisoprene.

F. General analysis of mill fiber samples.

In reality, residue analysis is difficult, and there are unforeseen complications. For example, if these residues go through the bleach plant, we can expect modifications of the chemical structure to complicate their analyses. This was observed on natural rubber¹² and polystyrene¹⁹. Analysis of spots on paper indicates that wax can be extracted, but polymers cannot. The heat from the dryer section "sets" the polymer, probably as a result of crosslinking reactions, and prevents its extraction by solvents. Similarly, solvent extraction of oven-dried fiber samples gave less extract than that of air-dried fiber samples during a study of the efficacy of secondary fiber cleaning equipment. In general, temperatures above 40°C should be avoided when trying to isolate white pitch deposits.

Solvent extraction of dry fiber samples can be used to help solve residue problems before they occur. For example, the efficiency of secondary fiber cleaners in terms of white pitch removal can be checked by taking samples at appropriate points, drying the sample at room temperature with air circulation such as in a laboratory hood, extracting the samples with solvent, and analyzing the residue after evaporating the solvent. For dilute fiber samples, rotary evaporation below 40°C is effective for concentrating the sample before analysis for white pitch.

G. Analysis of actual mill residues

Figure I-10 shows a general method for sample preparation and analysis. White pitch samples from 15 mills were collected and analyzed by the methods outlined. Table I-3 shows a general description of white pitch samples. Stickies from secondary fiber often contain hot-melt adhesives. Hot-melt adhesives contain wax, resin, polymers such as ethylene vinyl acetate (EVA), or mixtures of these components with many possible combinations^{37,38}. Many of the samples collected from mills showed characteristic ¹H-NMR peaks of ethylene vinyl acetate²¹, wax by gas chromatography, and a resin identified by gas chromatography or NMR. Figure I-11 shows the ¹H-NMR spectrum of common components of hot melt adhesive. Ethylene vinyl acetate is a dominant component of hot melt adhesive. Also other chemical shifts of wax and modified resin acids verified with gas chromatography are present at 0.78 and 3.90 ppm, respectively. The relative composition of the EVA ran from about 5% to 75% vinyl acetate groups with different distributions of molecular weight. Another sample analyzed by ¹H-NMR spectroscopy was quickly identified as fatty acids with some silicone resin or oil and a small aromatic peak. The aliphatic-silicone functionalities give characteristic peaks in the region between 0.05 ppm and 0.6 ppm. In this case, at 0.07 ppm and 0.55 ppm, gas chromatography analysis showed one major peak corresponding to a C-20 to C-22 fatty acid; the extract identity could have

been determined by mass spectrometry or by trying suitable standards, including suspect additives used at the mill. There were some samples of hydrocarbon polymers. A sample from a mill using secondary fiber showed polyisobutylene with the characteristic $^1\text{H-NMR}$ peaks at 1.11 ppm and 1.41 ppm, with a small peak at 5.3 ppm indicating residual unsaturation. Two other peaks at 0.89 ppm and 1.26 ppm were due to RCH_2R (Figure I-12); since SEC gave one peak corresponding to a molecular weight above 200,000 daltons, the sample was probably an ethyleneisobutylene copolymer. A small amount of polymethyl methacrylate was also present. Abietic acid, wax and monodisperse polystyrene were used as authentic samples to identify each component separated by SEC. Another sample from a mill using 100% deinked, bleached secondary fiber for tissue and towels was cis-1,4-polyisoprene with the $^1\text{H-NMR}$ spectra (Figure I-6) reported previously¹² with a SEC trace as shown in Figure I-5. A third sample was a polymer of polybutene with wax - possibly a hot melt or contact adhesive formulation. As seen in Table 1-4, primary sources of the contamination seem to be single side pressure sensitive tapes such as masking tape, clear tapes, fabric tapes, etc., double-faced splicing tapes such as those used by mills and converters, and hot melt adhesives in such application as book bindings and box sealants. In office waste, the sources of contaminants are not only tapes but also pressure sensitive labels and self seal envelopes. For mills not using

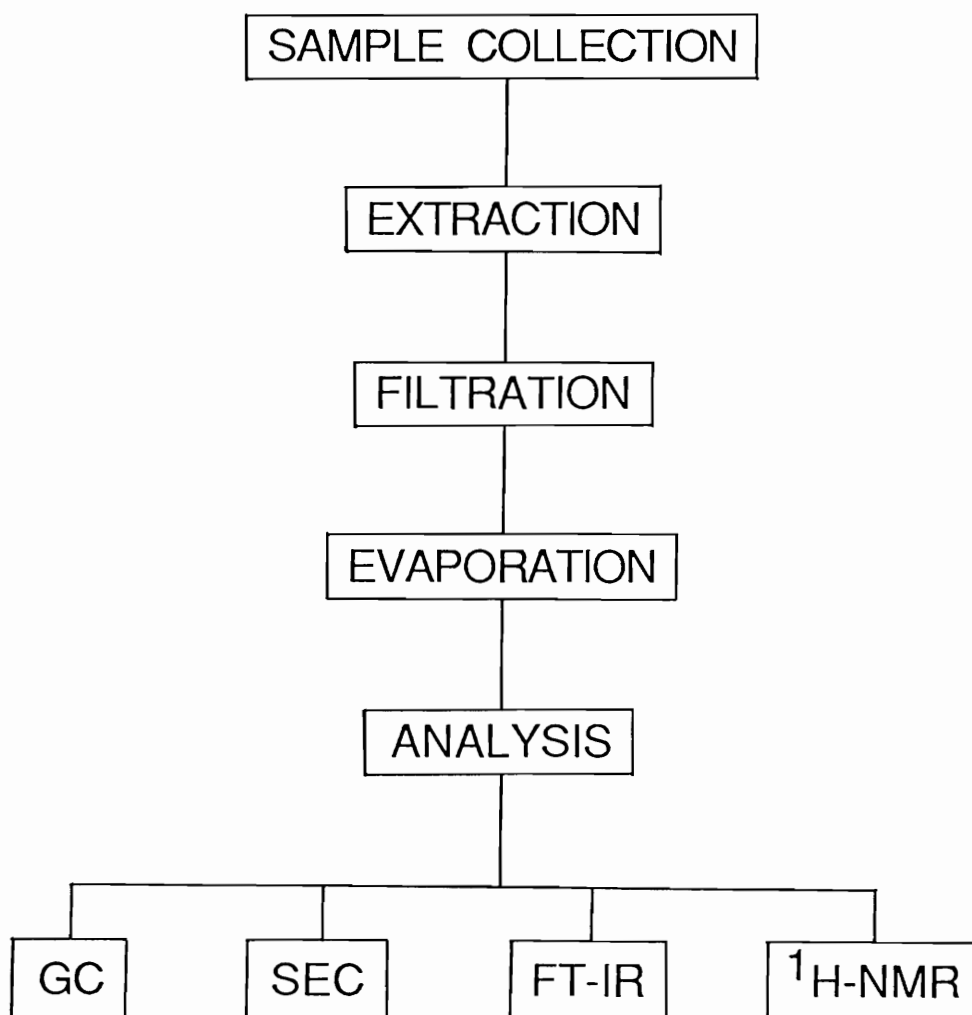


Figure I-10. Sample preparation and analysis.

Table I-3. General description of white pitch deposits.

Sample	Descriptions	Major Products
A	Black and gum-like sticky from dryer	Tissue paper, towel napkins
B	Tan fibrous layers with black and film-like layers	Linear board
C	Layer with black and brown color	Printing paper
D	Tan fibrous mass	Linear board
E	Tan fibrous mass	Linear board
F	Brown mass with white fiber	Tissue paper, napkin Bathroom tissue
G	Brittle mass with grey and white color	Tissue paper
H	Green brittle mass	Tissue paper
I	Black fibrous mass	Tissue paper
J	Brown solid mass with fiber	Tissue paper
K	Wire sample	Corrugating medium recycled paper
L	Wire sample	Linear board
M	Wire sample	Linear board
N	Sticky mass	Linear board
O	Wire sample	Corrugating medium recycled paper
P	Dryer felt sample	Corrugating medium recycled paper
Q	Wire sample	Corrugating medium recycled paper
R	Felt sample	Toilet tissue recycled paper

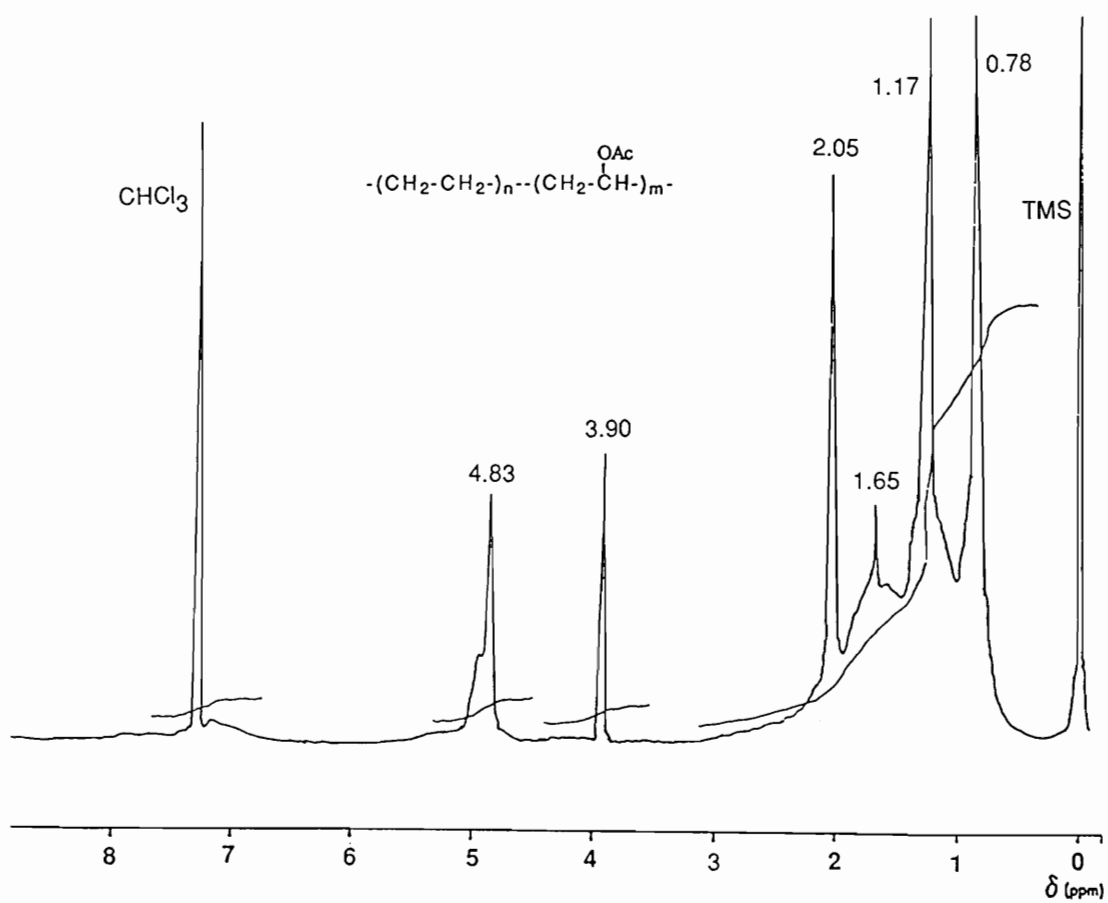


Figure I-11. $^1\text{H-NMR}$ spectrum of hot melt adhesive.

secondary fiber, most paper machine deposits come from wood pitch or additives used in the process. In one case, the residue was observed to contain wood pitch, but another residue from the same mill was mostly rosin, presumably used as a sizing agent. Gas chromatography is the most effective tool for detailed analysis of wood pitch, whereas the other methods do not give much useful information on these complex sample. Figure I-13 is a gas chromatogram of rosin used as sizing agent in the mill showing very strong intensity at 14.475. On the other hand, gas chromatogram of rosin in wood pitch gives only weak intensity at this region. Therefore gas chromatography can be used to trace the origin of contaminants. Even in such mills, polymers are sometimes found among the white pitch contaminants, indicating that an internal source of contamination must not be ruled out without proper analysis of the situation.

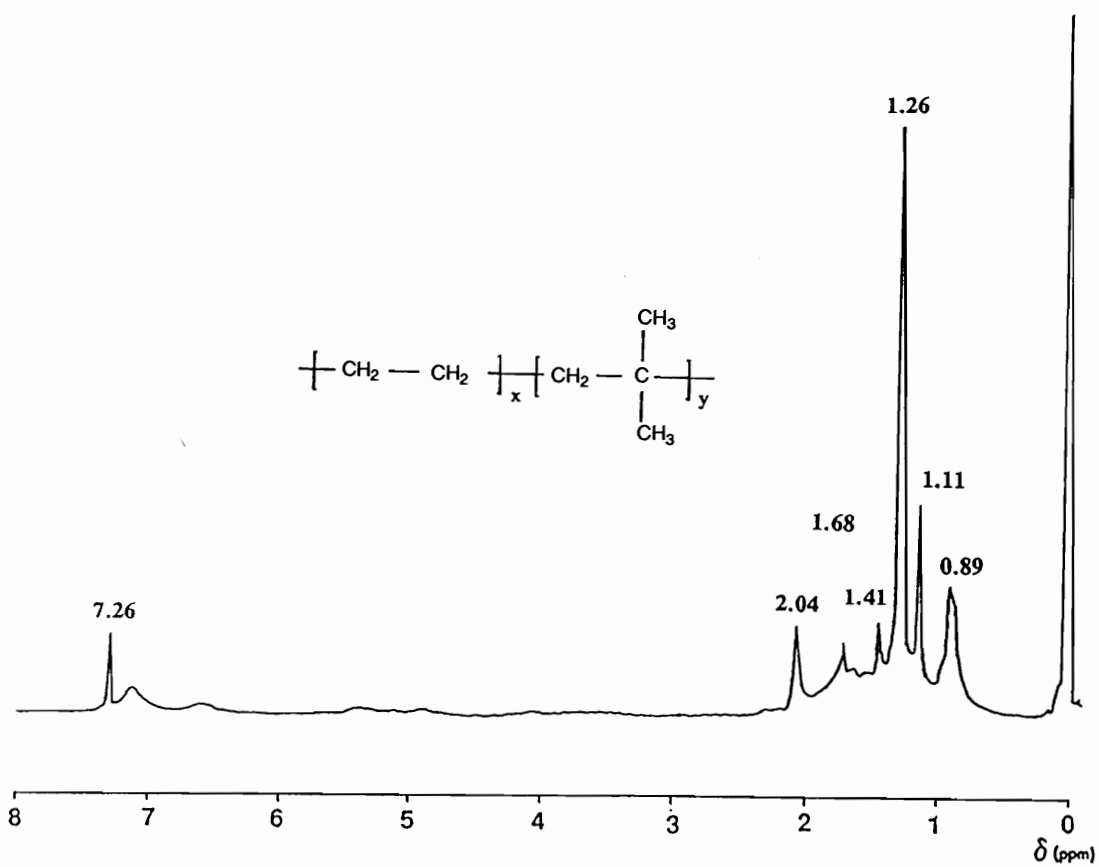


Figure I-12. $^1\text{H-NMR}$ of ethyleneisobutylene copolymer.

Table I-4. Major contaminants and possible sources of white pitch deposits.

Sample	Major Contaminants	Possible Sources
A	Cis-1,4-polyisoprene	Masking tape splicing tape
B	Paraffin wax	Adhesive
C	Paraffin wax low MW polyethylene	Adhesive
D	Paraffin wax high MW aliphatic polymers	Adhesive
E	Abietic acid	Sizing agent
F	High MW PVA	Adhesive
G	Wax	Adhesive
H	Wax	Adhesive
I	Wax	Adhesive
J	Wax	Adhesive
K	Wax, resin acids	Adhesive
L	Wax, resin acids	Adhesive
M	Fatty acids, silicon oil	Additives
N	Wax, PVA (MW 2,000- 10,000)	Adhesive
O	EVA	Adhesive
P	Wax	Adhesive
Q	Wax	Adhesive
R	Polyisobutylene PMMA	Adhesive

MW : Molecular weight
PVA : Polyvinylacetate
EVA : Ethylenevinylacetate
PMMA : Polymethylmethacrylate

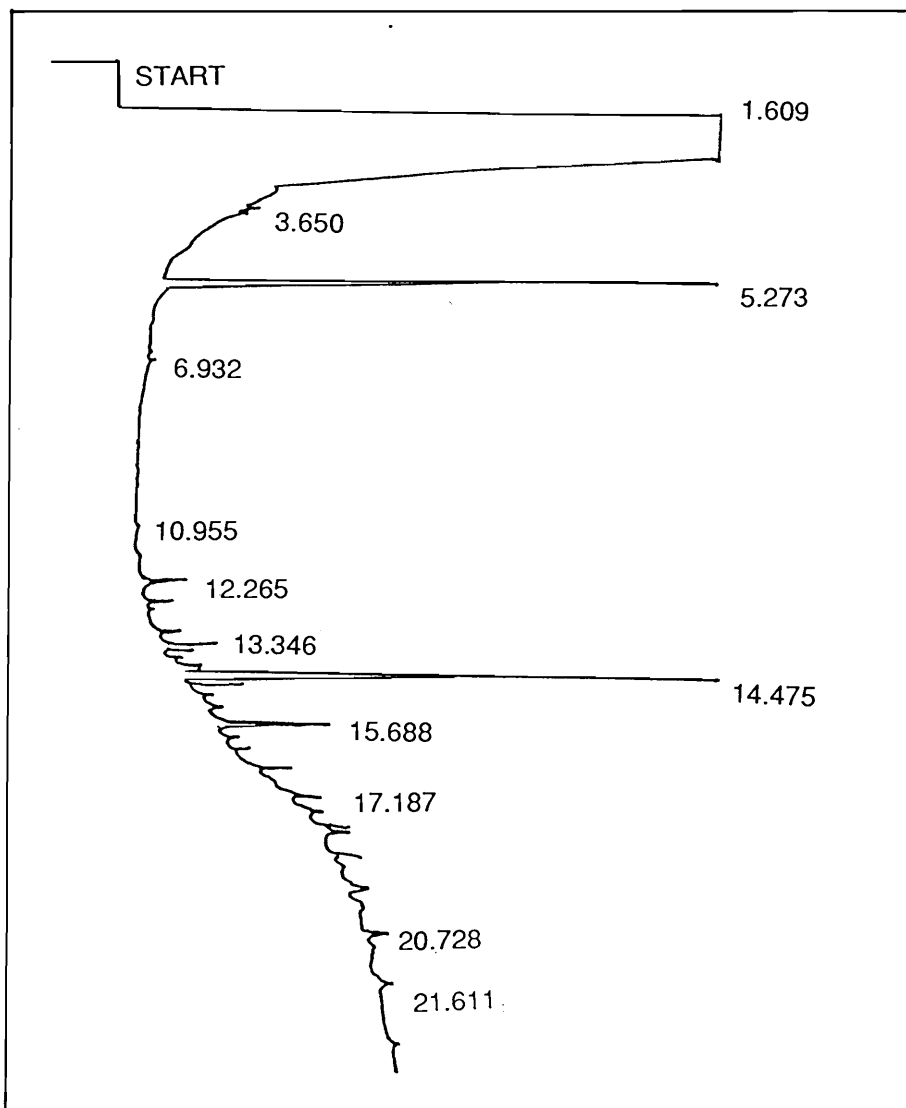


Figure I-13. GC chromatogram of rosin.

EXPERIMENTAL

General sample preparation and $^1\text{H-NMR}$ spectroscopy of the samples were carried out as detailed previously¹. Silylation is carried out by reacting 10-15 mg of deposit in a screw-cap vial with a septum with 1 ml of Tri-Sil/BSA in pyridine (Pierce) and heating at 70°C for 2 h. Heptadecanoic acid (1 mg) may be added prior to silylation as an internal standard⁶. Separation as in Figure I-2 is achieved with a 3% OV-17 column (2 m long with an internal diameter of 2 mm), raising the temperature from 90°C to 300°C at the rate of 10°C/min. Detection was by mass spectrometry. A capillary column was also quite effective for silylated samples³⁹.

Wax analysis was carried out by dissolving 50 mg of residue in 0.5 ml of toluene. Hexane (2 ml with internal standard) was added to precipitate polymer. A portion of the decanted liquid was taken for gas chromatography analysis. Gas chromatography separation, as in Figure I-4, was achieved by a 30-m-wide bore (0.75 mm), glass capillary column with SPB-5 bonded phase (Supelco), using a temperature program of holding at 100°C for 4 min, raising at 16°/min to 320°C, and holding for 4 min. Hydrogen was used as the carrier gas at 60 cm/min. Detection was by flame ionization.

Size exclusion chromatography was carried out using a 100-angstrom pore size ultrastyrigel column (Waters), with toluene as the eluent at 1.00 ml/min. A refractive index

detector was used. Molecular size calibration was carried out with monodisperse polystyrene standards, sucroseoctaacetate, wax, and other materials.

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CHAPTER II

Grafting of Maleic Anhydride Copolymers onto Cellulose Acetate and Methyl Cellulose

LITERATURE REVIEW

A. Chemistry of grafting reactions.

Grafting reactions of cellulose and its derivatives began in the early 1950's. By reacting cellulose molecules with synthetic monomers and polymers, it was hoped that hybrid materials with advantages of both constituents would be formed. Although there are hundreds of papers and patents published on the subject, there is negligible commercialization of grafting processes of cellulose. This is true because, with few exceptions, preparation of cellulosic graft copolymers involves free-radical polymerization methods¹⁻³. This process has several disadvantages : (1) the grafted polymer has a high molecular weight (meaning little involvement of the cellulose) and a polydisperse molecular weight distribution, (2) reproducibility of this method is poor, and there is little control over the grafting process, (3) there is much homopolymer formation. The net result is that grafting involves only a few high molecular weight molecules with a low level of graft substitution; consequently, the properties of the graft copolymers are not sufficiently different from a physical blend of the materials to warrant

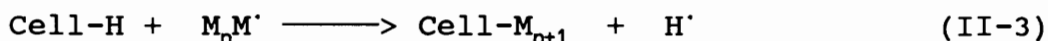
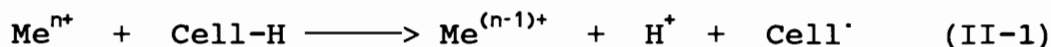
the expense of the grafting process. These problems have been reviewed in detail by Stannett⁴.

The reason that a low degree of cellulose fiber involvement and high molecular weight side chains are obtained is due to the free radical reaction in conjunction with the heterogeneous conditions of the reaction. When grafting onto cellulose fibers (that is the side chain is first formed and then added onto the cellulose backbone) via free radical polymerization occurs, there is a fast polymerization reaction rate, a strong possibility for termination of the growing side chain leading to the formation of homopolymer, and a slow reaction rate of the free radical in solution with the solid cellulose fiber. Even activation of cellulose fibers with reactive groups leads to the same problems. Thus, this technique will always have some limitations when used with solid cellulose fibers. Even in the case of cellulose acetate in solution, side chains below a molecular weight of 50,000 are difficult to produce.

This study illustrates one characteristic desired in a grafting technique. The reactive group or groups of the side chain should be stable in solution and react only with the cellulose fiber substrate. Under these conditions, the slow reaction rate under heterogeneous reaction conditions can be tolerated.

Various free-radical reactions differ mainly in the method of preparation of the free radical. These include

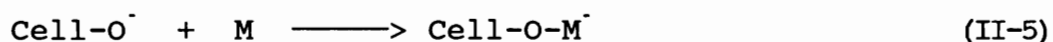
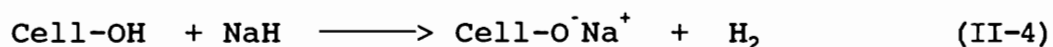
ionizing radiation (ultraviolet, X-rays, and gamma radiation), chemical redox systems (ferrous ion and hydrogen peroxide), and chemical modification of groups on the cellulose (xanthate group). The specific initiation reactions have been reviewed recently⁵. Equation (II-1) shows how metal ions with high oxidation potentials (Ce^{+4}) form free-radicals on the surface of cellulose (Cell-H) which in turn initiate polymerization of a vinyl monomer (M) as shown in equation (II-2). Equation (II-2) is an example of a "grafting from" reaction where the backbone polymer has an active site which induces polymerization. Due to chain transfer reaction, some polymerization is induced by free radicals not on the cellulose chains. Some of these will graft according to equation (II-3). Equation (II-3) is an example of a "grafting to" reaction because the side chain polymer is in an activated state and reacts with the backbone polymer.



A further limitation to free radical techniques is common to all of these techniques. There is only one active site per side chain. Certainly crosslinking agents such as divinyl benzene could be added, but this would lead to the

quick formation of a gel in the solvent phase causing more problems than are solved.

The "grafting from" reaction has also been used to form graft copolymers of cellulose by anionic polymerization techniques^{6,7}. A strong base such as NaOH or NaH is used to form an anion on the cellulose which induces polymerization of monomer in an inert solvent such as THF, DMSO, or DMF. The method is not very successful because the anions which are formed on the cellulose are limited to relatively weak alkoxides which do not readily induce polymerization. Furthermore, the reaction is carried out under heterogeneous reaction conditions which also makes polymerization difficult. The technique is summarized in equations (II-4) and (II-5).



Preparation of a polymer with a suitable end group, which then reacts with another backbone polymer, allows much greater control of the grafting process. This general approach was used by Avny and Schwenker by means of an acylation reaction⁸. They formed carboxy-terminated polystyrene by anionic polymerization techniques. They then formed the acid chloride of the polystyrylcarboxylic acid. The acid chloride was then reacted with preswollen cotton at 80°C for

24 hours in dry benzene using pyridine both as a catalyst and an acid scavenger. Although the process was very complicated, grafting yields (the fraction of preformed polymer which attaches to the cellulose backbone) were less than 10%. Besides being complicated, this method had the limitation of one reactive group per side chain and a group reactive with the solvent (or actually traces of water in the solvent).

In a much later study, Mansson and Westfelt⁹ reacted the acid chloride of polystyrylcarboxylic acid with cellulose acetate in tetrahydrofuran (THF) using pyridine or 4-dimethylamino pyridine (DMAP) as a catalyst. Although similar to the method of Avny and Schwenker, this reaction had the advantage of being carried out under homogeneous reaction conditions with a very powerful catalyst, giving grafting yields up to 83%. However the method has the disadvantages of requiring rigorous exclusion of water during the grafting reaction, requiring numerous reaction steps, and only one or two reactive sites per chain are possible.

Narayan and Tsao¹⁰ attempted to use the nucleophilic properties of the living polystyryl carbanion as a nucleophile to displace methanesulfonate (mesylate) groups from mesylated cellulose acetate (Figure II-1). However the polystyryl carbanion is so basic that little of the polystyrene attaches; mostly, homopolymer is formed due to proton abstraction from hydroxyl groups or water, reaction with the carbonyl of the acetate groups, or abstraction of methyl

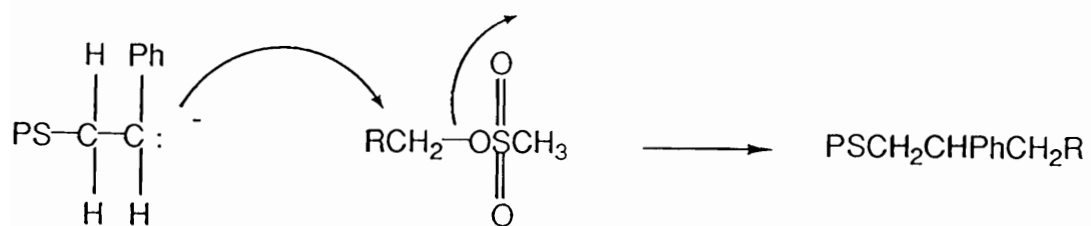


Figure II-1. Reaction scheme for grafting polystyryl carbanion onto mesylated cellulose acetate.

protons adjacent to the carbonyl of the acetate group (analogous to the first step of a Claisen condensation reaction) by the strongly basic anion. Even capping the polystyryl carbanion with 1,1-diphenylethylene (the extra benzene ring stabilizes the anion, making it less basic) led to the same problem.

More recently Biermann and Narayan have published reports of novel grafting reactions onto soluble cellulose derivatives and related reactions^{11-14,36,37}. The reaction involved nucleophilic displacement of the mesylate group by the carboxylate nucleophile under homogeneous reaction condition using organic solvents. Briefly, polymers with carboxylate groups were reacted with mesylated cellulose derivatives. Much more detailed discussions on previous grafting reactions are available^{2,14,16}.

There are some works in the literature using grafting or substitution reactions on soluble forms of cellulose^{5,17}. In the case of the xanthate method, good grafting yields are possible; however, the method still has the drawback that only a few high molecular weight side chains are obtained. The use of new solvents for cellulose¹⁷⁻²⁰ offers the potential for preparation of graft copolymers using the methods developed by our research group but these have not yet been explored.

B. Chemical modification of cellulose fibers.

The chemistry of cellulose fiber modification is relevant to this work. Many such modifications are commonly used in the pulp and paper industry. These reactions, or more precisely similar reactions, will be used to attach synthetic fibers onto cellulose fibers with complete control over the reaction. One example is the use of the alkyl ketenes dimers (AKD) as sizing agents in the paper industry. Recent work²¹ shows that these dimers form β -ketoester linkages with the hydroxyl groups of cellulose. In analogous reaction alkenyl succinic anhydride (ASA) is used as a sizing agent. In this case the reaction is an esterification reaction of the anhydride functionality of the ASA²². This reaction is depicted in Figure II-2.

The reaction of acetic anhydride and acetyl functionalities under a variety of conditions with cellulose is well known^{23,24}. More powerful catalysts such as N-methylimidazole^{25,43} (NMID) or 4,4-dimethylamino pyridine (DMAP)^{26,44} with catalytic activities about 360 and 17,000 times greater than pyridine, respectively, have received little attention for chemical modification of cellulose.

C. Use of acid anhydride functionality with acylation catalysts.

Anhydride moieties are easily incorporated into polymers by copolymerization with maleic anhydride. Use of the powerful

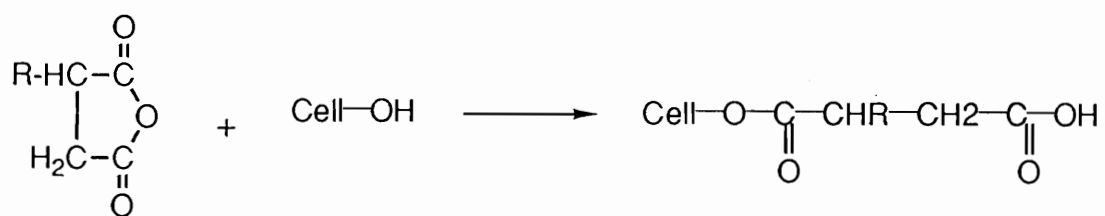


Figure II-2. Reaction of ASA with cellulose.

acylation catalysts described above should give good grafting yields. This reaction is analogous to addition of ASA to cellulose (Figure II-2) during the sizing of paper²². The number of reaction sites per side chain is easily controlled by the amount of maleic anhydride employed.

INTRODUCTION

Mankind has suffered from the shortage of natural resources - especially raw materials based on petrochemical resources and thus has tried to develop the substitutes for the shortage. In that sense cellulose is the most important resources which can be in part used for the replacement of such raw material because it is the most abundant²⁷ and the most economical organic renewable resources available.

The major cell wall constituents of wood are cellulose, hemicellulose, and lignin. Cellulose is the most basic cell wall material in the whole plants, serving as the structural material by which plants, trees, as well as grasses sustain the strength to stay upright. The cellulose content of wood is usually in the range of 41-51%²⁸.

Cellulose is used in the form of cotton, paper, regenerated cellulose, cellulose derivatives, and wood. It is generally accepted^{29,30} that cellulose is a highly oriented crystalline, and a linear macromolecule composed of D-anhydroglucopyranose units (often abbreviated to anhydroglucose units or even to glucose units for convenience) linked together β -1,4 glycosidic bonds with a degree of polymerization (DP) which varies from 1,000 to 15,000 depending on its origin and the extent of possible degradation during its isolation. The numbering of the carbons in the anhydroglucose units is in Figure II-3. Cellulose has one primary

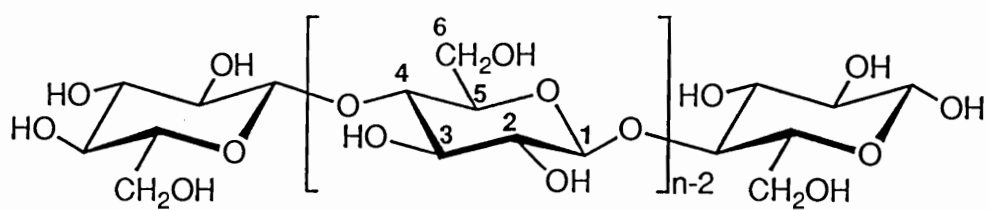


Figure II-3. Structure of the cellulose molecule.

hydroxyl group at C₆ and two secondary hydroxyl groups at C₂ and C₃ per anhydroglucose unit. Thus cellulose can undergo esterification - acetylation, nitration, and xanthation -, etherification - alkylation and benzylation -, replacement of -OH by NH₂ and halogenation, replacement of -H in -OH by Na, oxidation of -CH₂OH to -COOH, and oxidation of secondary -OH groups to aldehyde and carboxyl.

Increase in the price of petroleum have focused attention on the potential uses of cellulose for a new class of materials with specific and improved properties for a wide range of application. Considering the potentiality of cellulose as an alternative resources of organic matter, extensive studies on the preparation, properties, and applications of cellulose graft copolymers have been carried out to impart specially valuable properties deficient in natural cellulose since the early 1950's³¹⁻³³.

Grafting of synthetic polymers onto cellulose and its derivatives is a useful way to improve the qualities of both materials and to expand the range of their applications². Graft copolymerization has a number of unique features. A graft copolymer consists of a main polymeric backbone to which one or more chains of another polymeric species is grafted, i.e., covalently linked. In the context of this review, the main chain would be cellulose and cellulose derivatives, and the grafted side chain could consist of virtually any other polymer. It is therefore apparent that,

unlike random or block copolymers, grafting is a suitable technique for modifying cellulose or cellulose derivatives. It is also clear that grafting cannot greatly modify the properties of the existing backbone polymer since only a few linkages are involved. Rather, it is a technique for adding the properties of one polymer to those of another polymer with a minimum of perturbation of the properties of the main component polymer. For instance, grafting of polyacrylonitrile gave cellulose wool-like appearance and improved resistance to microorganisms³⁵. Grafting of a fluorine-containing polymer and polymethylvinylpyridine (phosphate form) imparted water-, oil-, and flame-resistant properties to cellulose, respectively^{35,36}.

Many hundreds of papers and patents have been published since the early 1950's. In spite of this intense effort, there has been relatively little application of cellulose graft copolymers. The reason for the lack of commercialization have been in part economic and in part the inability of polymer scientists and engineers to find alternative methods to achieve comparable properties³⁷. To date, there are a few reaction schemes that attempt to prepare graft copolymers of cellulose with the goal of preparing a new material with the advantages of both materials. Most of the proposed grafting reactions are carried out by free radical mechanisms^{1,2,5}. Some inherent disadvantages in these procedures are a high percentage of occluded homopolymer in the graft product which

may be difficult to remove from the grafted copolymer, only a few high molecular weight graft molecules, poor reproducibility of reaction results, and low levels of substitution. The net result is that grafting involves only a few high molecular weight molecules with a low level of graft substitution; consequently, the properties of the graft copolymers are not different from a physical blend of the materials to warrant the expense of the grafting process. These problems have prevented significant commercialization of grafting processes and have been reviewed in detail by Stannett⁴.

A high degree of control over the grafting process can be achieved by nucleophilic substitution reactions. Biermann et al. have reported that polystyrylcarboxylate, polyamide carboxylate, and poly(methylmethacrylate)carboxylate were grafted onto mesylated cellulose acetate with a high level of control by nucleophilic displacement of the mesylate groups by carboxylate anions^{11,36}. Recently, Biermann and Narayan grafted poly(ethyleneimine) onto mesylated cellulose acetate by second order nucleophilic displacement of mesylated groups by amine groups³⁷.

Anhydrides react with alcohols by the acylation reaction mechanism in which $-OOCR$ is replaced by another basic group such as RO^- of ROH . This study describes a simple and effective way to achieve a high level of control over the grafting reactions of ethylene/maleic anhydride copolymer (EMA) or styrene/ maleic anhydride copolymer (SMA) onto

cellulose acetate (CA) or methyl cellulose (MC) by the acylation reaction mechanism under homogeneous reaction conditions. The reaction sites per side chain is easily controlled by the amount of maleic anhydride copolymer employed. Heterogeneous reaction is generally slow compared to homogeneous reaction because strictly limited reaction (penetration) of chemicals occurs just at the fiber surface. The products generated by heterogeneous grafting reaction contain less than one branch per cellulose chain³⁸⁻⁴² and the chain length of the grafts tend to be quite large. These phenomena have been attributed to the inaccessibility of the crystalline regions of cellulose to the reagents. Acylation reaction itself is not new. However, its application to the formation of cellulose graft copolymer is novel.

Pyridine is commonly used in acylation reactions where it serves as a nucleophilic catalyst⁴³ and base to accept the generated proton. More powerful catalysts like N-methylimidazole (NMID) and 4-(N,N-dimethylamino)-pyridine (DMAP) can be employed to accelerate the acylation rate. The relative catalytic efficiency of pyridine, NMID, and DMAP for the catalyzed acetylation of isopropyl alcohol is 1:360:17000 (pyridine:NMID: DMAP)^{25,26,43,44}. Figure II-4 shows the mechanism for the DMAP-catalyzed grafting reaction.

Crosslinking is to be expected since many reaction sites on the maleic anhydride copolymers could potentially react with the numerous hydroxyl groups on the cellulose deriva-

tives. The crosslinks will principally involve the C-6 hydroxyl groups, since cellulose acetate often has many of the free hydroxyl groups at the C-6 position and there is less steric hindrance for formation of ester linkages at this position. Rowland also found that C-6 hydroxyl groups are favored in esterification reaction⁴⁵. Figure II-5 shows the formation of crosslinks by the reaction of maleic anhydride copolymers with cellulose derivatives.

RESULTS AND DISCUSSION

Grafting reactions were accomplished by reacting either cellulose acetate (CA) of 2.4 degree of substitution (DS) and methyl cellulose (MC) of 1.8 degree of substitution with high molecular weight ethylene/maleic anhydride copolymer (EMA) and high molecular weight styrene/maleic anhydride copolymer (SMA) by the acylation reaction mechanism (Figure II-4). In order to achieve high grafting efficiencies, these grafting reactions were carried out under strictly anhydrous conditions to avoid hydrolysis of the anhydrides. The addition of 0.1% and 0.2% water in dry DMF did not change the gelation time significantly of the ethylene/maleic anhydride copolymer-cellulose system; however, the use of reagent grade, undried DMF of unknown moisture content did increase the gelation time and lead to a softer gel. The reaction of 2.5% (w/vol) ethylene/maleic anhydride copolymer or styrene/maleic anhydride copolymer with 5% (w/vol) cellulose acetate or 3.3% (w/vol) methyl cellulose in DMF at 50°C resulted in the formation of a solid gel, indicating crosslinking of the chains of the cellulose derivatives and the maleic anhydride copolymers. There is no method given for observing the crosslinking other than gelation. Size exclusion chromatography (SEC) cannot be used to determine the molecular-weight distribution because the gelled product is not soluble. Similarly, nuclear magnetic resonance (NMR) techniques

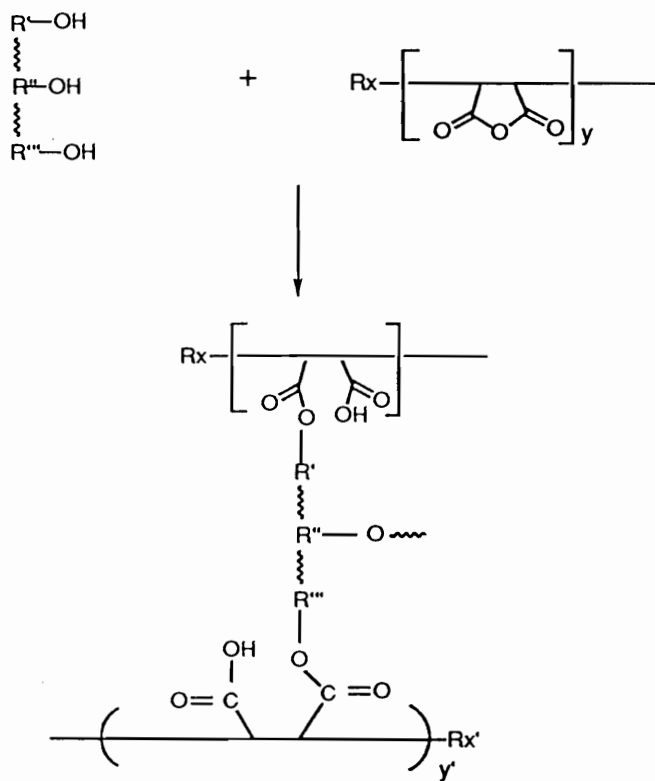


Figure II-5. Formation of the cross-linked graft copolymer by reaction of maleic anhydride copolymer with cellulose derivative.

available to us could not be used for the same reason. Even fourier transform infrared (FTIR) characterization of the products was inconclusive due to the small extent of reaction during the grafting reaction. Solvent extraction was used to remove unreacted maleic anhydride copolymer as an indication of grafting.

The gelation time of ethylene/maleic anhydride copolymer onto cellulose acetate is much shorter than that of styrene/maleic anhydride copolymer. This difference in gelation time may be due to steric hindrance and the slightly lower viscosity of the styrene/maleic anhydride copolymer. The styrene/maleic anhydride copolymer contains a bulky phenyl group where ethylene/maleic anhydride copolymer has a hydrogen atom. Each gelation time is reported in Table II-1.

Two cellulose acetates (Lot# A8A and A18B of the same commercial product of Kodak Co.) were used for the acylation reaction with ethylene/maleic anhydride copolymer and showed different acylation reaction time of 3 minutes and 20 minutes, respectively. Although no readily apparent explanation for these discrepancies is available, lot# A18B was used for further experimentation because of unavailability of additional samples of lot# A8A. Even though these two cellulose acetate have been reported to have the same nominal molecular weight (61,000), the viscosity measurements were substantially different between these lots. Because the gelation time of EMA onto Ca of the Aldrich co. is inconve-

Table II-1. Results of the grafting reaction at 50°C in DMF.

Catalyst	Copolymer	Substrate	Gelation time
Pyridine	EMA	CA	12 hrs
	SMA	CA	>10 days
NMID	EMA	CA	65 min
	SMA	CA	570 min
DMAP	EMA	CA ^k	20 min
	EMA	CA ^a	60 min
	SMA	CA	210 min
DMAP	EMA	MC	15 min
	SMA	MC	90 min

EMA : Ethylene/maleic anhydride copolymer

SMA : Styrene/maleic anhydride copolymer (Average M.W. 350,000)

DMAP : 4-(N,N-dimethylamino)pyridine

NMID : N-methylimidazole

CA^a : Cellulose acetate (Aldrich co, catalog #18,085-5)

CA^k : Cellulose acetate (Kodak co, Lot# A18B)

MC : Methyl cellulose (Kodak co.)

niently much longer (60 minutes) than that of EMA onto CA of the Kodak co., only the Kodak CA was used to compare the acylation reaction time using different catalysts.

The acylation reactions of 3.3% (w/vol) methyl cellulose in DMF with maleic anhydride copolymers occurred faster than that of 5% (w/vol) cellulose acetate, as would be expected, because of the higher viscosity and lower degree of substitution of the methyl cellulose, which gives more reactive sites for copolymerization. Table II-2 shows the results of viscosity measurements of the starting materials.

Considering the high molecular weights of the polymers involved, an extent of reaction of less than 10% would certainly give a crosslinked product. For example, while the 1700 molecular weight SMA has about 6 reactive anhydride units per molecule, gelation was not observed even after 7 days of reaction at 50°C with DMAP catalyst. Considering that the acylation of isopropyl alcohol is complete within 5-10 min at 54-70°C with 2% DMAP, one would expect crosslinking with the low molecular weight styrene/maleic anhydride copolymer⁴⁴.

It is known that weak bases are effective catalysts for the reaction of an anhydride with an alcohol to form an ester⁴⁶. Acylation reactions often use pyridine as a catalyst. Acylation reactions in the presence of pyridine probably involve initial acylation of pyridine followed by a reaction with the alcohol^{47,48} and the reaction times tend to

Table II-2. Viscosities of starting materials.

Material	MW	Concentration	Viscosities (cps)
CA (Kodak-A)	61,000	2.7% in Acetone	245
CA (Kodak-B)	61,000	7.6% in Acetone	137
CA (Aldrich)	30,000	7.6% in Acetone	20
MC (Kodak)	86,000	1.1% in DMSO	249
EMA (Aldrich)	Unknown	12.3% in DMF	130
SMA (Aldrich)	350,000	12.3% in DMF	108

MW : Molecular weight

Kodak-A : Lot# A8A

Kodak-B : Lot# A18B

be inconveniently long. DMAP was used as catalyst to accelerate the rate of esterification since it forms a more stable pyridinium ion by resonance stabilization^{26,44}. The formation of this stable ion results in an effective increase of the acylation reaction rate. As shown in Table II-1, the reaction times are considerably decreased with NMID and DMAP catalysts. The acylation reactions of cellulose acetate (1.0 g) with ethylene/maleic anhydride copolymer (0.5 g) in the presence of DMAP (0.4 g) in DMF (20 ml) with, or without, pyridine (0.5 g) did not change the gelation time significantly, meaning the amount of DMAP used was sufficient to act as an acid scavenger.

Grafting yields (%) were calculated as the weight percentage of copolymer that is covalently linked to the cellulose backbone of the graft copolymer, determined after DMF extraction. The DMF extraction removes unreacted maleic anhydride copolymers and DMAP present in the reaction products. The increase in weight of the products obtained after DMF extraction, compared to the original weight of cellulose acetate and methyl cellulose, indicated that grafting has occurred. Grafting yields increased with the use of NMID and DMAP, and most of the yields were 70-95%.

EXPERIMENTAL

A. Materials

N,N-dimethylformamide (DMF) was freshly distilled under vacuum over CaH_2 before use and transferred by syringe technique under dry nitrogen. Cellulose acetate (CA) of 2.4 degree of substitution (Eastman Kodak co., Rochester, NY, catalog no. 1173335) was used for this experiment. Methyl cellulose (MC) of 1.6 to 1.9 degree of substitution (Eastman Kodak co., Rochester, NY, catalog no. 1374875) was also used as a substrate. Ethylene/ maleic anhydride copolymer (EMA) (Aldrich co. Milwaukee, WI, Catalog no. 18,805-0) and styrene/maleic anhydride copolymers (SMA) (Aldrich Co. catalog no. 18,293-1, Average M.W. 350,000, styrene content 50% and catalog no. 30,267-4, average M.W. 1,700, anhydride content 33%) were dried in a vacuum desiccator over phosphorous pentoxide. The viscosities of starting materials were measured with the Brookfield Viscometer (Model DV-1).

B. Grafting Reaction

The grafting reaction was carried out using 0.5 g of maleic anhydride copolymers, either 1 g of cellulose acetate in 20 ml of N,N-dimethylformamide (DMF), 1 g of methyl cellulose in 30 ml of DMF, and the catalysts. Pyridine (0.5 ml), N-methylimidazole (NMID) (0.5 ml), and 4-(N,N-dimethyl amino)pyridine (DMAP) (0.3 g) were employed as catalysts and

gelation time was determined for each reaction. Grafting reactions were carried out under strictly anhydrous conditions to avoid hydrolysis of the anhydride. The reaction mixtures were reacted at 50°C with shaking. After the reaction periods, several of the reaction mixtures were extracted several times with DMF to remove unreacted copolymers and DMAP. The extract was dried in a vacuum oven at 50°C and weighed. Extractions were carried out until no further unreacted copolymers and DMAP were obtained. An extraction period of 72 hours at 50°C was sufficient to extract almost completely. Grafting yields were calculated as the weight percentage of the copolymers which are attached to the cellulose derivative backbones, which is given by:

$$\text{Grafting yield} = \frac{\text{weight of copolymer in grafts}}{\text{weight of copolymer used}} \times 100\%$$

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